

# THE EFFECTS OF CATIONS ON PULVERIZED COAL COMBUSTION

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## INTRODUCTION

Although coal has been burned for centuries, many fundamental aspects of the process remain poorly understood. Conflicting theories appear in the voluminous combustion literature. There is, however, general agreement that coal combustion occurs in two stages: pyrolysis or devolatilization of the coal followed by heterogeneous combustion of the char (1-3). In most practical combustors, the latter acts as the rate determining step for the overall process. For more efficient coal combustion, therefore, it is essential to understand the parameters which most affect the rate of heterogeneous char combustion.

Char combustion rate depends primarily on the reactivity of the carbonaceous material to oxygen. This reactivity is controlled by several parameters such as gas diffusion rates to and from the reactive surface and catalysis of combustion by inorganic species present in the char. This research concentrates on the effect of various inorganic species on the rate of pulverized lignite combustion.

Jenkins et al. (4) have shown that the reactivity of coal chars is rank related. Chars from low rank coals such as lignites were found to be more reactive than chars produced from high rank bituminous coals. This has been attributed to the presence of inorganic constituents, in particular ion exchangeable cations, in low rank coals and their chars (5-7).

Walker (7) and McKee (8) have shown that alkali and alkaline-earth metals are catalysts for the carbon-oxygen reaction. Furthermore, the predominant ion exchangeable cations on American lignites are alkali (Na, K) and alkaline-earth (Ca, Mg, Ba) metals (9). Therefore, it is possible that highly dispersed cations on low rank coal chars catalyze the heterogeneous combustion step.

Reactivity data have been generated previously under isothermal conditions in the absence of particle ignition (5-7). The present work reports on lignite combustion under nonisothermal conditions. It was directed primarily towards understanding the effects of cations (K, Ca, Na) on the initial stages of pulverized coal combustion.

## EXPERIMENTAL

Sample Preparation. The ion exchangeable cations located on the carboxyl groups of a Texas lignite (PSOC-623) were removed by acid washing with 0.04 M HCl. Alkali (Na, K) and alkaline-earth (Ca) metals were back exchanged on the acid-washed coal using 1 M metal acetate solutions. Details of the procedure are outlined elsewhere (10). The quantity of exchanged cations was determined by atomic absorption spectroscopy.

Combustion Experiments. Raw and modified lignite (mean weight particle size 62  $\mu\text{m}$ ) were combusted in an entrained-flow reactor at an initial furnace (gas and wall) temperature of 973 K. The reactor configuration and operating principle have been well documented (10-12). Weight loss rate data were obtained using an ash tracer technique.

## RESULTS AND DISCUSSION

Sample Characteristics. Proximate analyses of the raw and modified Texas lignite are shown in Table 1. Acid washing with HCl reduced the total ash yield

TABLE 1

PROXIMATE ANALYSES OF TEXAS LIGNITE (PSOC 623)

	<u>Ash, wt% (Dry)</u>	<u>VM, wt% (Dry)</u>	<u>Moisture, wt%</u>
Raw	15.9	44.7	10.8
Ca Loaded	14.0	46.5	8.0
Na Loaded	13.0	43.4	12.3
K Loaded	15.0	43.9	12.4
Acid-Washed	10.7	46.1	7.7

of the coal by 33 wt%. Subsequent addition of the cations increased the ash yields by between 18% (Na) and 29% (K), based on the raw lignite. The quantity of each cations back exchanged, wt% dry basis, is shown in Table 2. The acid washing was

TABLE 2

CATION LOADINGS ON THE LIGNITE\*

<u>Cation</u>	<u>wt% (Dry)</u>	<u>milliequivalents/g of coal (Dry)</u>
Ca	3.8	1.2
Na	2.6	1.0
K	5.0	1.1

\* The acid-washed sample had less than 0.1 wt% (dry) cations on the coal.

an efficient procedure since less than 0.1 wt% (dry basis) of the cations remained on the acid washed coal.

Weight Loss Rate Data. Figure 1 illustrates weight loss rate data (wt%, daf) in air for raw and exchanged lignites. Residence times were determined using the model formulated by Morgan (10). Essentially, the model accounts for slip velocity between particles and flowing gas.

In the initial 0.1 s, the acid-washed lignite had the greatest rate of weight loss. The initial step in the combustion process accounting for weight loss is pyrolysis. Figure 2 illustrates the effect of cations on the rate of pyrolysis. These data were obtained in N<sub>2</sub> at a furnace temperature of 973 K. During pyrolysis, the acid-washed lignite had a greater rate of weight loss and a greater total weight loss in the residence time of the reactor. It is suggested that cations catalyze secondary char forming reactions of the primary volatiles, particularly the tars (10). These cracking and/or polymerization reactions on the surface of particles reduced the initial rate of weight loss (when tar evolution was predominant) and the total yield of volatiles due to surface carbon deposition.

As shown in Figure 1, when heterogeneous combustion predominated (residence times >0.1 s) the modified coals lost weight more rapidly than the acid-washed lignites. Alkali and alkaline-earth metals are known to be excellent catalysts for the carbon-oxygen reaction (7,8). Hence, it is suggested that cations exchanged on the coal catalyzed the heterogeneous combustion of the char.

The Na and K loaded lignites underwent greater total weight loss (by about 20 wt%) than the calcium loaded lignite in the total residence time of the furnace. Isothermal reactivity data have shown that K and Na are better catalysts than Ca for the carbon-oxygen reaction (5,7). However, the low weight loss by the Ca loaded coal may be the result of a combination of two factors: catalysis of secondary reactions and catalysis of the carbon-oxygen reaction.

#### SUMMARY

The effect of cations on the combustion behavior of pulverized lignite can be divided into three main areas: the rate of weight loss due to pyrolysis, the total weight loss due to pyrolysis and the rate of heterogeneous char combustion. The presence of cations (Na, K, Ca) reduced the rate of pyrolysis and the total weight loss due to pyrolysis but increased the char combustion rate.

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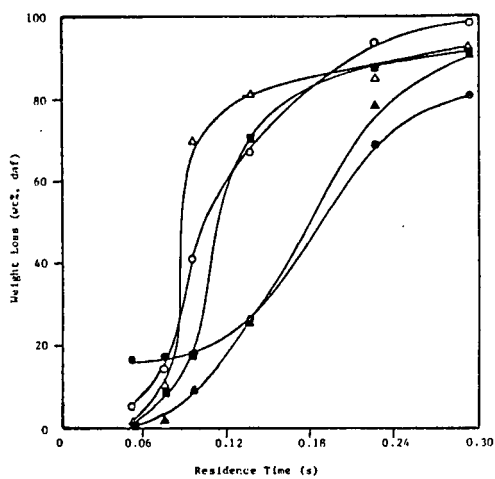


Figure 1. Effect of Cations on Combustion at a Furnace Temperature of 973 K. ■ Na; ○ K; ● Ca; ▲ Acid-washed; ▲ Raw.

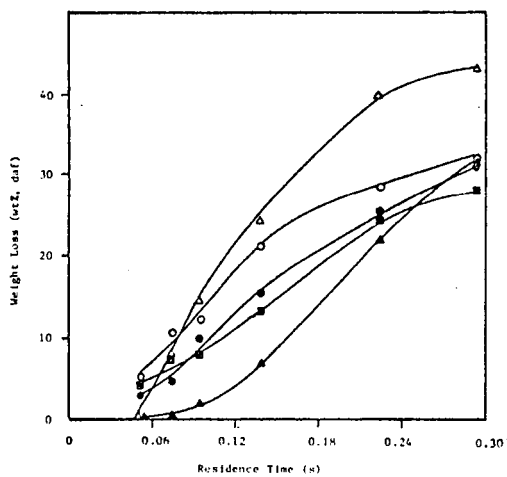


Figure 2. Effect of Cations on Pyrolysis in Nitrogen at 973 K. ■ Na; ○ K; ● Ca; ▲ Acid-washed; ▲ Raw.